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Ugaji et al.

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(54) **LITHIUM SECONDARY BATTERY**

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USPC 429/212, 231.95
See application file for complete search history.

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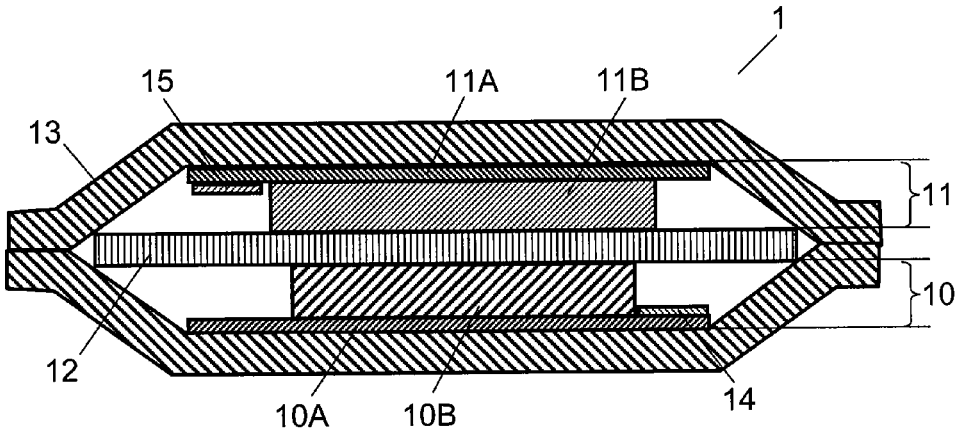
(57) **ABSTRACT**

A negative electrode of a lithium secondary battery has a negative electrode active material including at least one element of silicon and tin. Capacities of the positive electrode and the negative electrode of the lithium secondary battery are set as follows. In a completely charged state of the lithium secondary battery charged by a predetermined charging method, the positive electrode active material and the negative electrode active material are in a first partially charged state, respectively. In a completely discharged state of the lithium secondary battery discharged by a predetermined discharging method, the negative electrode active material is in a second partially charged state.

1 Claim, 8 Drawing Sheets



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H01M 10/44	(2006.01)
H01M 10/0525	(2010.01)
H01M 4/02	(2006.01)

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FIG. 1

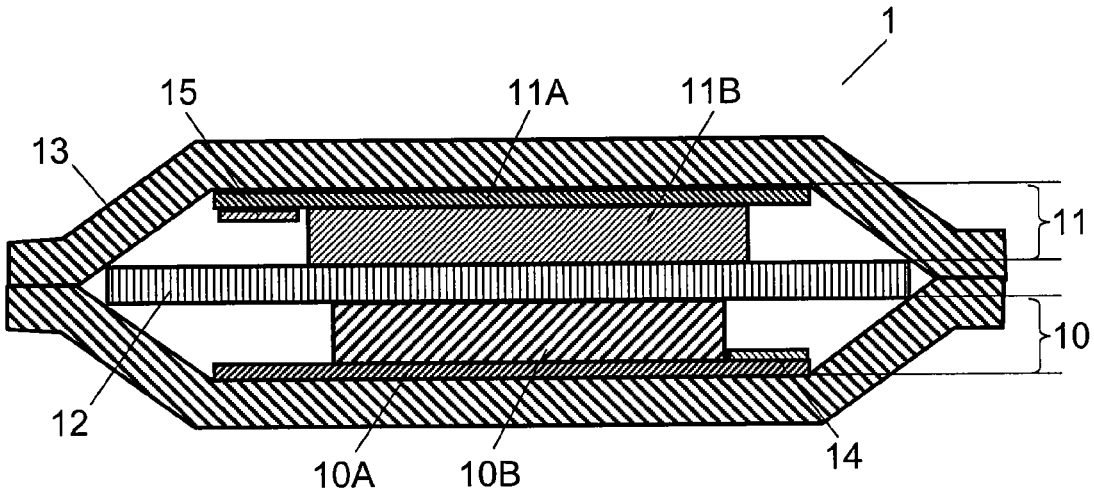

1
15
11A
11B
13
11
10
12
10A
10B
14

FIG. 2

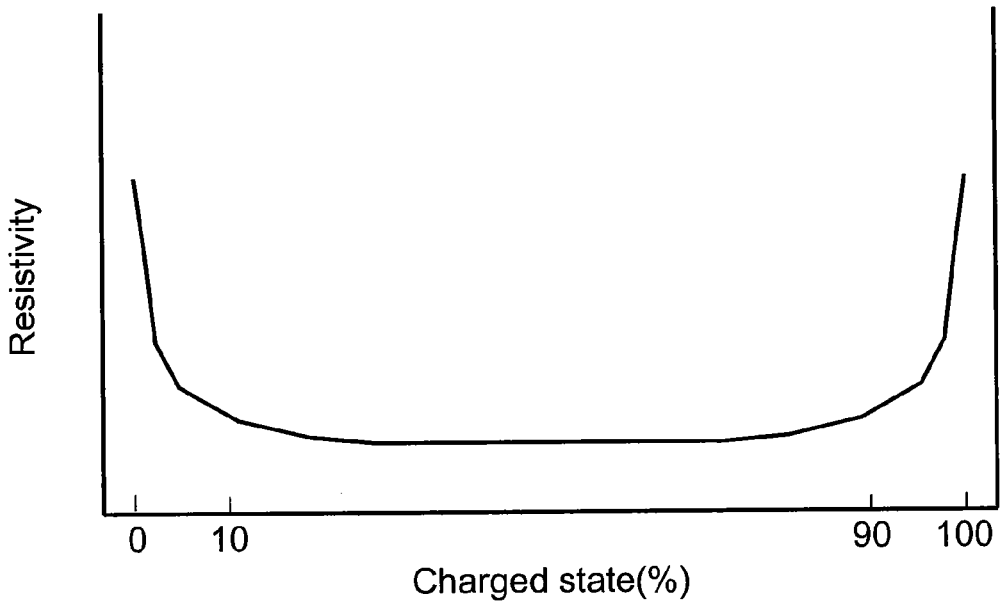

Resistivity
0
10
90
100
Charged state(%)

FIG. 3

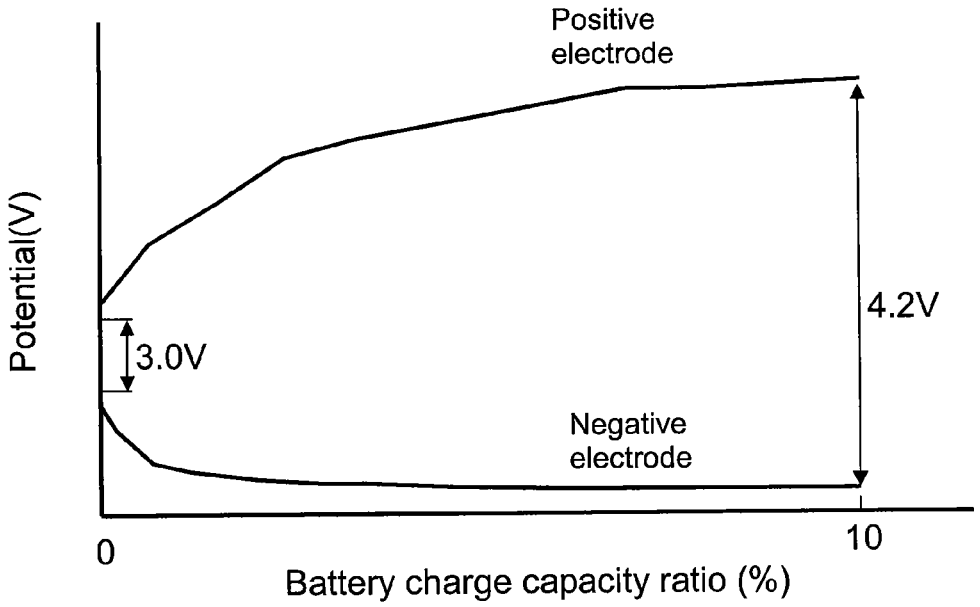

Positive electrode
Potential(V)
4.2V
3.0V
Negative electrode
0
10
Battery charge capacity ratio (%)

FIG. 4

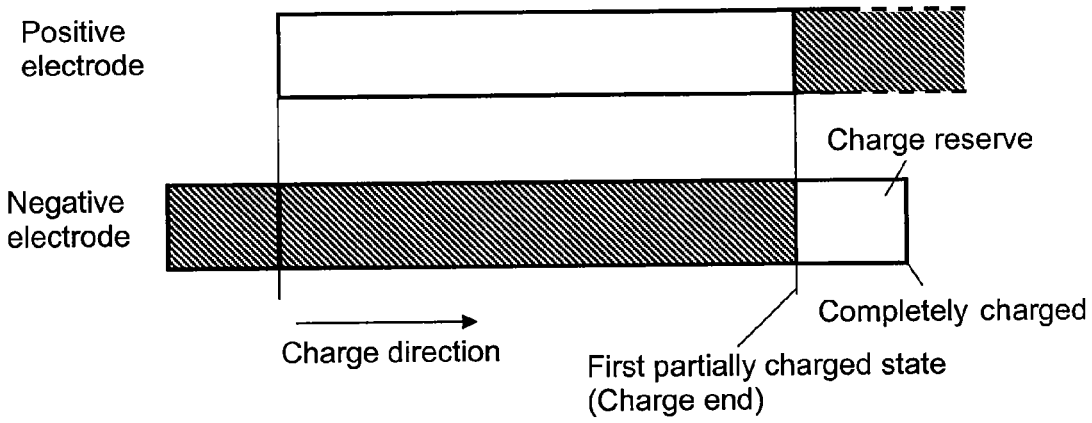

Positive electrode
Charge reserve
Negative electrode
Completely charged
Charge direction
First partially charged state
(Charge end)

FIG. 5

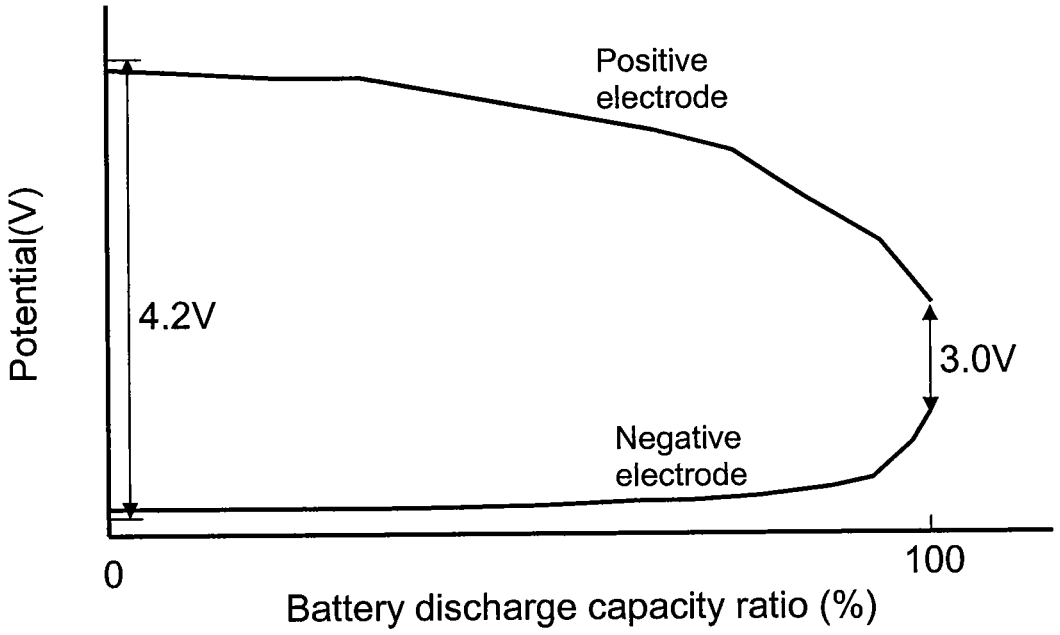

Positive electrode
Potential(V)
4.2V
3.0V
Negative electrode
0
100
Battery discharge capacity ratio (%)

FIG. 6

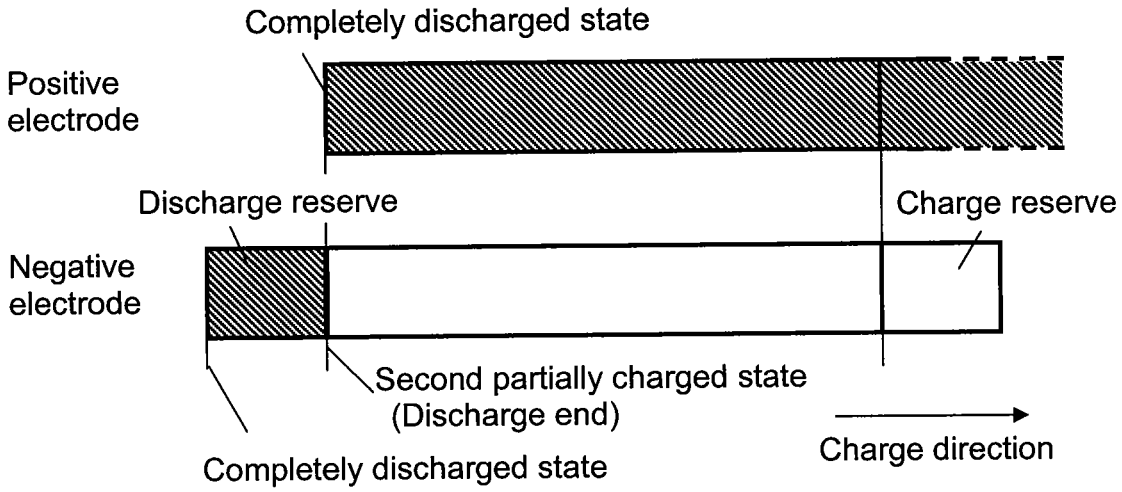

Completely discharged state
Positive electrode
Discharge reserve
Charge reserve
Negative electrode
Second partially charged state
(Discharge end)
Completely discharged state
Charge direction

FIG. 7A

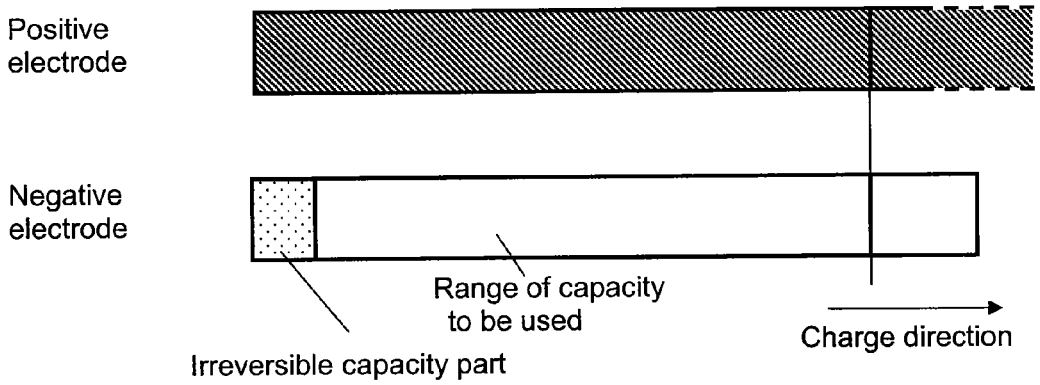


FIG. 7B

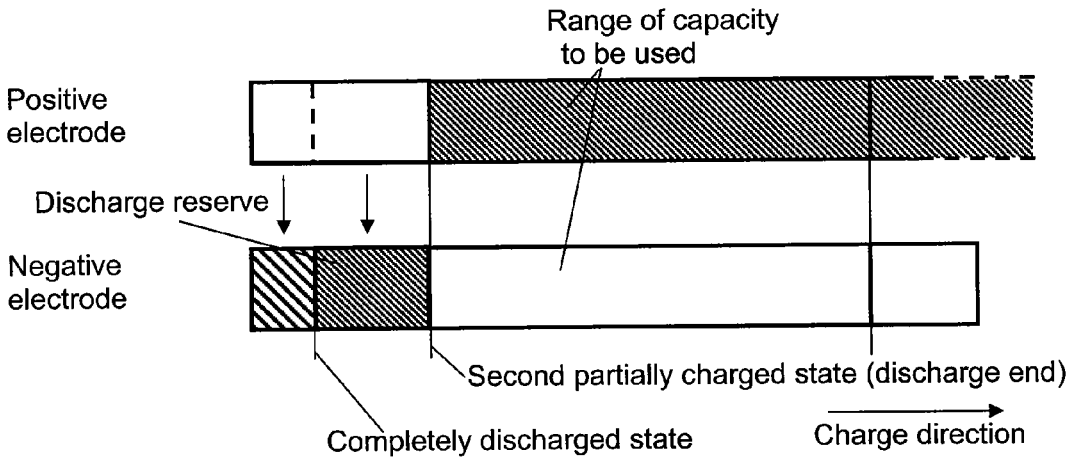


FIG. 8

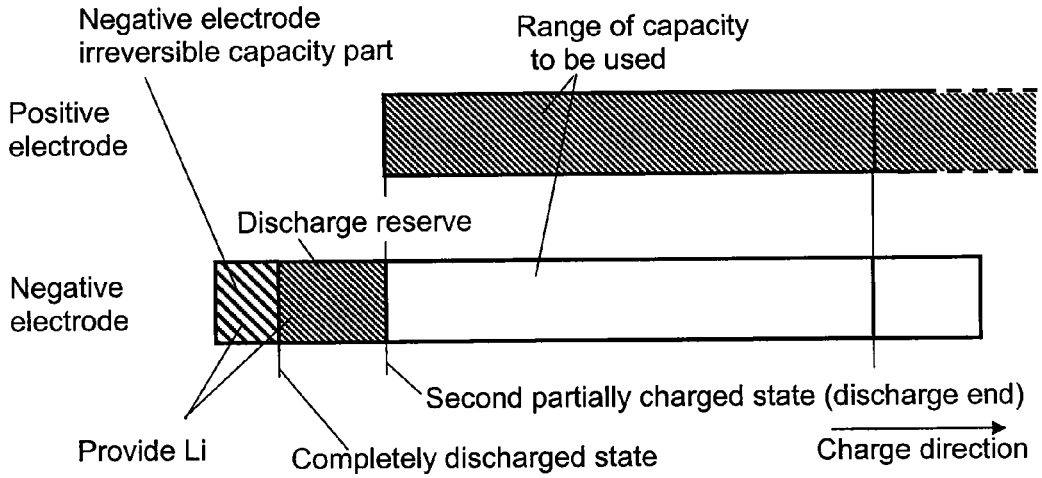


FIG. 9A

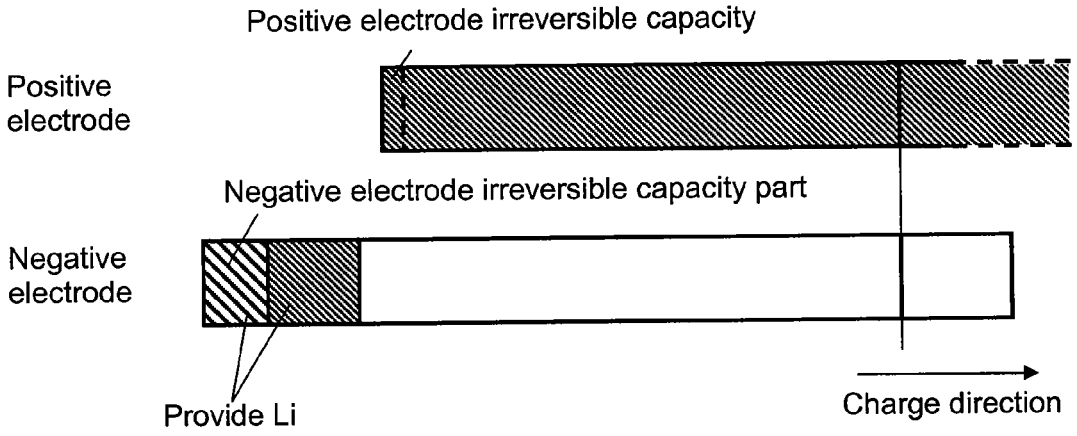

Positive electrode irreversible capacity
Positive electrode
Negative electrode irreversible capacity part
Negative electrode
Provide Li
Charge direction

FIG. 9B

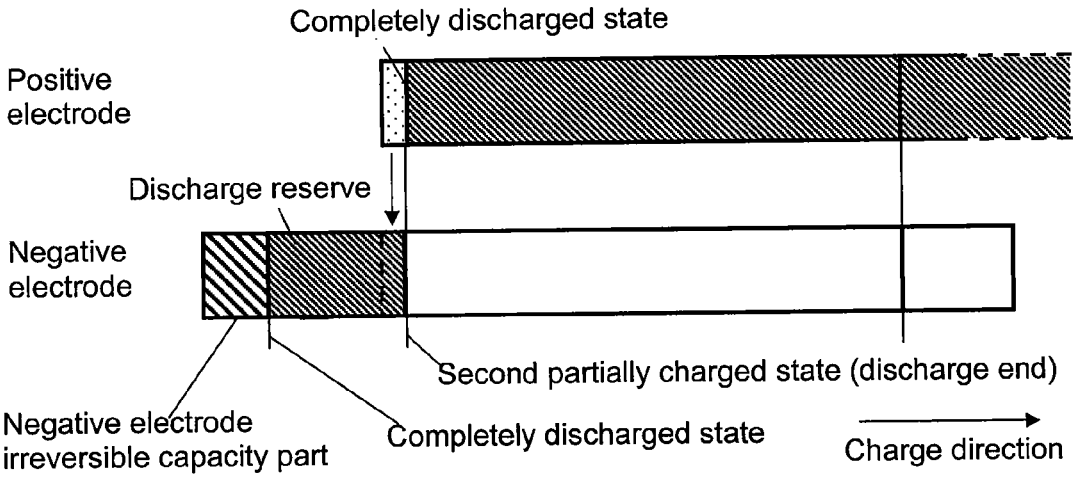

Completely discharged state
Positive electrode
Discharge reserve
Negative electrode
Second partially charged state (discharge end)
Negative electrode irreversible capacity part
Completely discharged state
Charge direction

FIG. 10

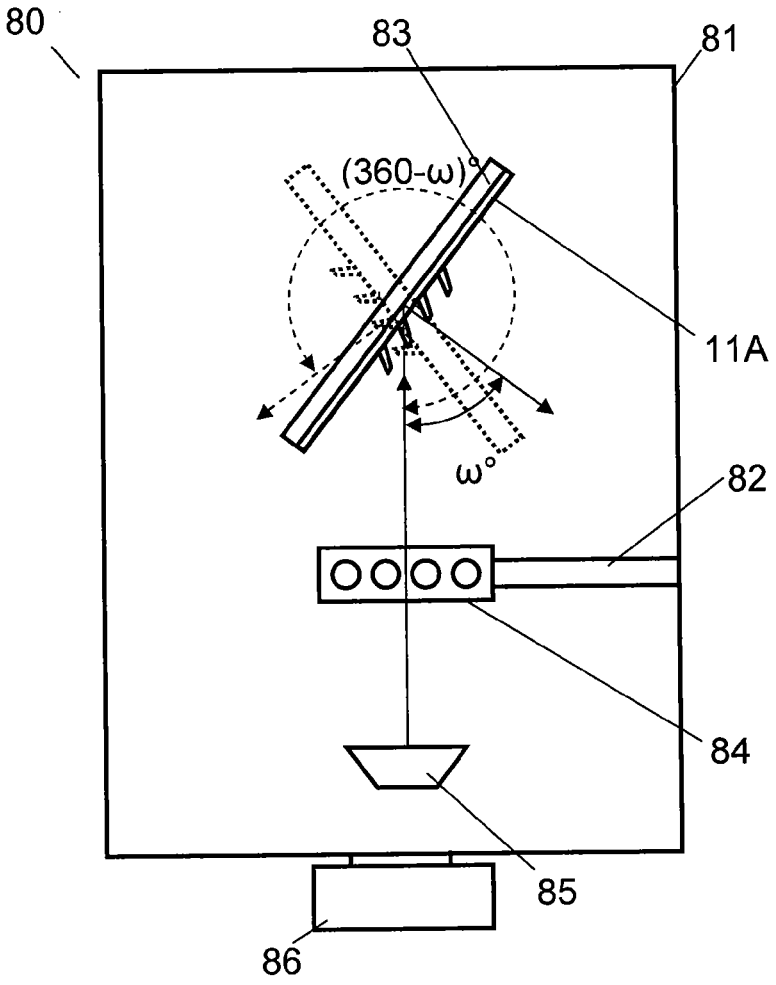


FIG. 11

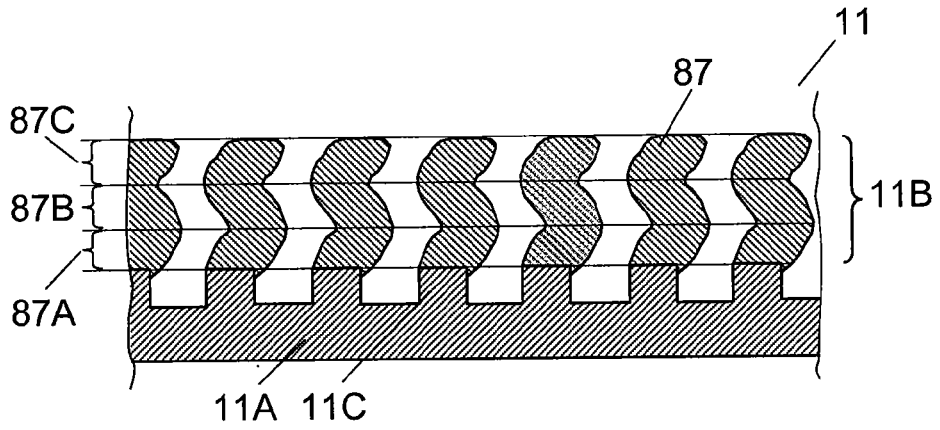


FIG. 12

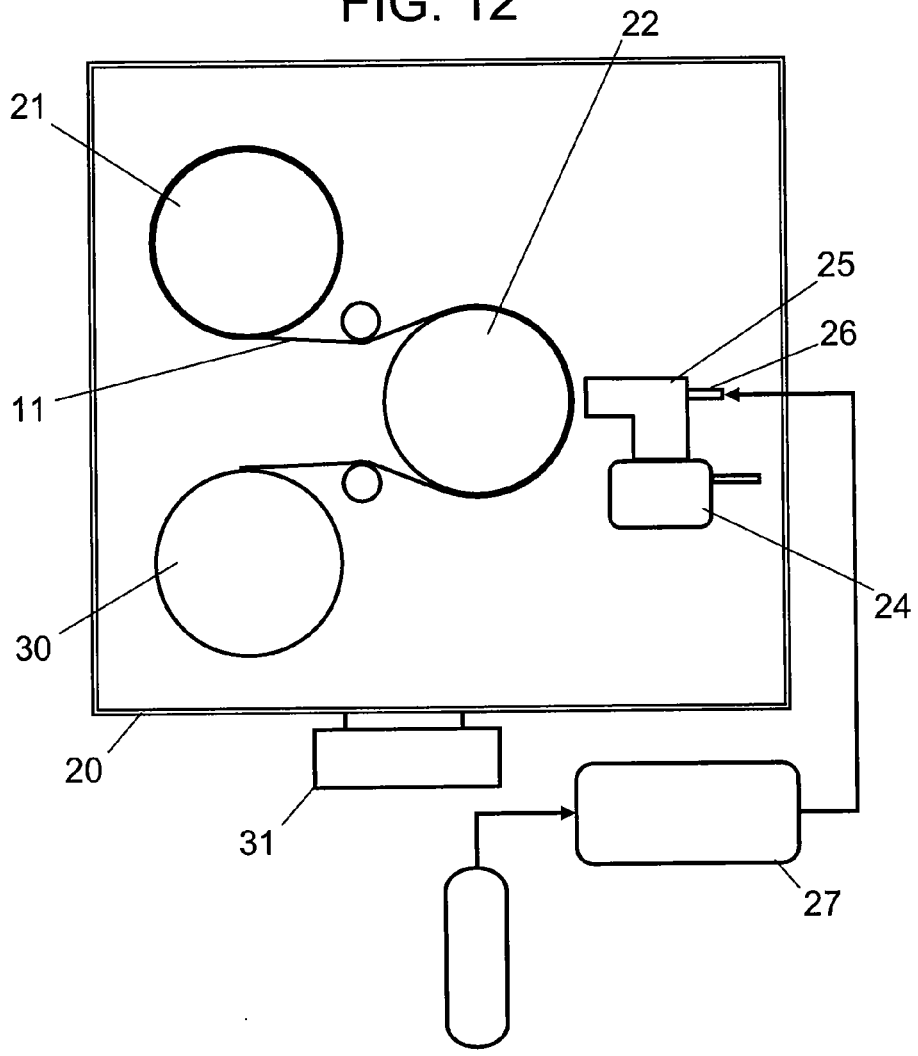


FIG. 13

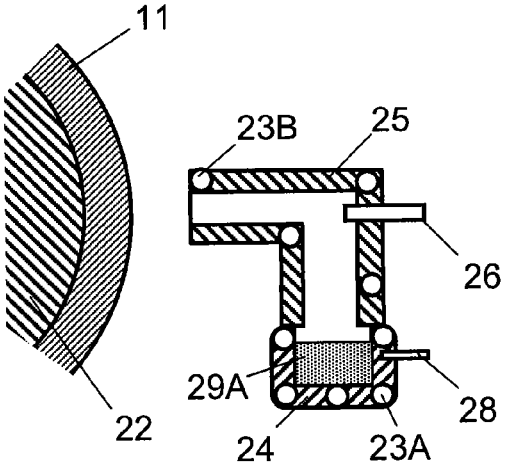
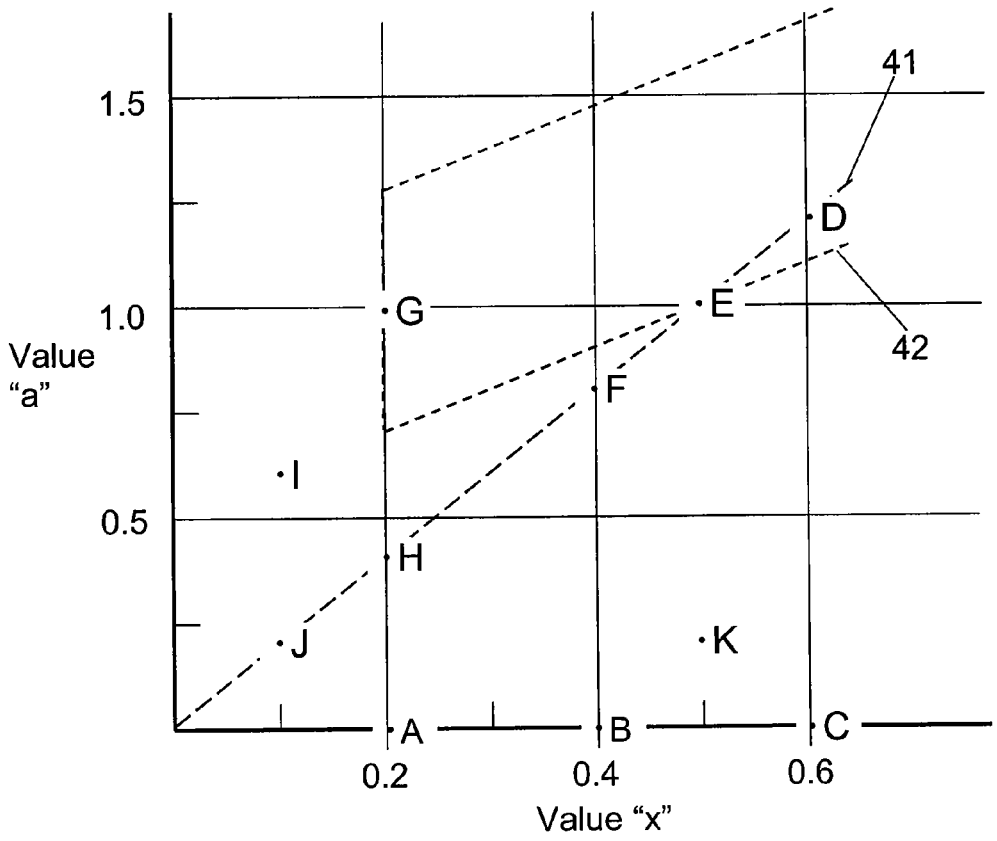


FIG. 14



LITHIUM SECONDARY BATTERY

TECHNICAL FIELD

The present invention relates to a lithium secondary battery having an active material including at least one element of silicon and tin in a negative electrode and being excellent in the charge/discharge cycle characteristics.

BACKGROUND ART

Recently, with the development of portable devices such as personal computers and portable telephones, batteries as a power source for such devices have been increasingly demanded. The batteries used for the above-mentioned applications are required to be used at ordinary temperatures as well as to have a large energy density and excellent cycle characteristics.

In order to respond to these requirements, for both positive electrode and negative electrode, active materials having a large capacity density have been newly developed. Above all, elemental substances, alloys, or oxides of silicon (Si) or tin (Sn) that can provide an extremely large capacity density are promising materials as negative active materials.

However, in lithium secondary batteries using these negative electrode active materials, sufficient charge/discharge cycle characteristics cannot be obtained. Specifically, silicon oxide "SiO_x (x=0.3)" is used as the negative electrode active material. Lithium cobaltate ($LiCoO_2$) used in a general lithium secondary battery may be used as the positive electrode active material. A mixture solution of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) containing lithium hexafluorophosphate ($LiPF_6$) may be used as an electrolyte. These are used so as to produce a winding type lithium secondary battery. When this battery is charged and discharged repeatedly in the conditions of charge and discharge current of 1.0 C, charge end voltage of 4.2 V and discharge end voltage of 2.5 V, large capacity deterioration occurs at about 100 cycles.

In order to avoid the above-mentioned problem, it is preferable that the discharge electric potential at the negative electrode is made to be as low as possible. For example, Patent document 1 discloses a lithium secondary battery using silicon oxide (SiO) as a negative electrode active material in which capacity deterioration associated with the charge/discharge cycle can be suppressed by controlling the discharge end electric potential of the negative electrode to 0.6 V or less with respect to a lithium reference electrode.

However, as in Patent document 1, when the lithium reference electrode is provided in the battery in order to control the discharge electric potential of the negative electrode using SiO with respect to the lithium reference electrode, the battery configuration becomes complicated, thus making practicability thereof difficult. In other words, a battery needs to have a third electrode terminal, in addition to a positive electrode terminal and a negative electrode terminal. Furthermore, when a charge/discharge cycle is repeated from the beginning of the charge/discharge cycle with less deterioration of the positive and negative electrode active materials, electric potential ranges in which both positive and negative electrodes are used are changed according to the deterioration of active materials of the positive and negative electrodes. Therefore, even if the discharge end voltage is set so that the discharge end electric potential of the negative electrode becomes 0.6 V or less based on the positive electrode, it is difficult to determine whether or not the discharge end electric potential of the negative electrode is maintained to be 0.6 V or less. Thus, it is difficult to suppress the capacity deterioration associated with the charge/discharge cycle by measuring a battery voltage so as to detect a charge and discharged state of the negative electrode.

Patent document 1: Japanese Patent Unexarmined Publication No. H11-233155

SUMMARY OF THE INVENTION

The present invention provides a lithium secondary battery having an active material including at least one element of silicon and tin in a negative electrode and being excellent in charge/discharge cycle characteristics.

The lithium secondary battery of the present invention has a positive electrode, a negative electrode and a non-aqueous electrolyte having lithium ion conductivity and being interposed between the positive electrode and the negative electrode. The positive electrode contains positive electrode active material absorbing and releasing lithium ions. The negative electrode contains negative electrode active material including at least one element selected from a group consisting of silicon and tin. Then, in a completely charged state of the lithium secondary battery charged by a predetermined charging method, the positive electrode active material and the negative electrode active material are in a first potentially charged state, respectively. Furthermore, in a completely discharged state of a lithium secondary battery charged by a predetermined discharging method, the negative electrode active material is in a second partially charged state. Thus, by combining the charged states of the positive electrode active material and the negative electrode active material, it is possible to suppress the capacity deterioration associated with the charge/discharge cycle. Thus, a battery is designed by combining the charged state of the positive electrode active material and the charged state of the negative electrode active material, and thereby a lithium secondary battery having excellent charge/discharge cycle characteristics can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic sectional view showing a lithium secondary battery in accordance with exemplary embodiments of the present invention.

FIG. **2** is a conceptual graph showing a relation between a charged state and the resistivity in a negative electrode of a lithium secondary battery in accordance with a first exemplary embodiment of the present invention.

FIG. **3** is a conceptual graph showing the change in electric potentials of the positive electrode and the negative electrode during the lithium secondary battery is charged.

FIG. **4** is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a charge end point in the lithium secondary battery.

FIG. **5** is a conceptual graph showing the change in electric potentials of the positive electrode and the negative electrode during the lithium secondary battery is discharged.

FIG. **6** is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a discharge end point in the lithium secondary battery.

FIG. **7**A is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode when the lithium secondary battery is assembled.

FIG. **7**B is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a discharge end point in the lithium secondary battery.

FIG. **8** is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a time of assembly or at a discharge end point of another lithium secondary battery in accordance with the first exemplary embodiment of the present invention.

FIG. **9**A is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a time of assembly of a further lithium secondary battery in accordance with the first exemplary embodiment of the present invention.

FIG. **9**B is a conceptual diagram showing a presence state of lithium ions in the positive electrode and the negative electrode at a discharge end point of the further lithium secondary battery in accordance with the first exemplary embodiment of the present invention.

FIG. **10** is a schematic configuration view showing a manufacturing device for a non-aqueous electrolyte secondary battery in accordance with a specific example of the present invention.

FIG. **11** is a schematic sectional view showing a negative electrode produced by using the device shown in FIG. **10**.

FIG. **12** is a schematic configuration view showing a vacuum evaporator for providing lithium to the negative electrode in accordance with the specific example of the present invention.

FIG. **13** is a conceptual sectional view showing a configuration of a lithium vapor deposition nozzle of the vacuum evaporator shown in FIG. **12**.

FIG. **14** is a graph showing a value "x" and a value "a" in the negative electrode of each sample in accordance with the specific example of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, exemplary embodiments of the present invention are described with reference to drawings. Note here that the present invention is not necessarily limited to the following contents.

First Exemplary Embodiment

FIG. **1** is a schematic sectional view showing a configuration of a laminated battery as an example of a lithium secondary battery in accordance with one exemplary embodiment of the present invention. In lithium secondary battery **1**, positive electrode **10**, negative electrode **11** and separator **12** intervened therebetween are laminated to each other so as to form an electrode group. This electrode group and a non-aqueous electrolyte (not shown) having lithium ion conductivity are accommodated inside outer case **13**. The non-aqueous electrolyte is impregnated into separator **12** and interposed between positive electrode **10** and negative electrode **11**.

Positive electrode **10** includes positive electrode current collector **10**A and positive electrode active material layer **10**B supported by positive electrode current collector **10**A. Negative electrode **11** includes negative electrode current collector **11**A and negative electrode active material layer **11**B supported by negative electrode current collector **11**A. Positive electrode active material layer **10**B generally includes a positive electrode active material, an auxiliary conductive material and a binder. However, it may include only a positive electrode active material. Also, negative electrode active material layer **11**B generally includes a negative electrode active material, an auxiliary conductive material and a binder. However, it may include only a negative electrode active material.

Positive electrode current collector **10**A and negative electrode current collector **11**A are coupled to one ends of positive electrode lead **14** and negative electrode lead **15**, respectively. Other ends of positive electrode lead **14** and negative electrode lead **15** are drawn out of outer case **13**, respectively.

Positive electrode active material layer **10**B includes a positive electrode active material capable of absorbing and releasing a lithium ion. An example of such a material may include lithium cobaltate ($LiCoO_2$), lithium nickelate ($LiNiO_2$), lithium manganate ($LiMn_2O_4$), and the like. However, the material is not necessarily limited to these examples. As positive electrode current collector **10**A, Al, an Al alloy, Ni, Ti, and the like, may be used.

Negative electrode active material layer **11**B includes a negative electrode active material including at least one element selected from the group consisting of silicon (Si) and tin (Sn). An example of such a negative electrode active material may include an elemental substance of Si and Sn, an oxide such as SiO_x ($0.05<x<1.95$) and SnO_y ($0<y\leq 2$), or an alloy or a compound or a solid solution obtained by substituting a part of the above-mentioned materials with at least one element selected from B, Mg, Ni, Ti, Mo, Co, Ca, Cr, Cu, Fe, Mn, Nb, Ta, V, W, Zn, C, N, and Sn, and the like. As a tin-containing material, Ni_2Sn_4, Mg_2SnSiO_3, LiSnO, and the like, may be used. These materials may be used singly or plural kinds of these materials may be used simultaneously. An example in which plural kinds of materials are used simultaneously may include a compound containing Si, oxygen and nitrogen, a composite of plurality of compounds containing Si and oxygen with constituting ratios of Si and oxygen varied, and the like. Among them, SiO_x ($0.05<x<1.95$) is preferred because it is relatively low price and has high stability.

For a non-aqueous electrolyte, various lithium ion conductive solid electrolytes or non-aqueous electrolytic solutions may be used. As the non-aqueous electrolytic solution, a non-aqueous solvent dissolving lithium salt is preferably used. As the non-aqueous electrolytic solution, a solution including a well-known composition may be used and the composition is not particularly limited.

Materials of separator **12** and outer case **13** are not particularly limited and may employ materials generally used in various forms of lithium secondary batteries.

The above-mentioned positive electrode active materials hold lithium ions in the crystal structure thereof in a discharged state, and the lithium ions are released by charging. However, when the charge depth is increased and the amount of released lithium ions are increased, the crystal structure is no longer maintained. Consequently, the crystal structure is destroyed, and lithium ions are no longer absorbed and released reversibly. Therefore, in a completely charged state of lithium secondary battery **1** charged by a predetermined charging method, the capacity is controlled so that the positive electrode active material is in a first partially charged state. By controlling in this way, the capacity deterioration of the positive electrode active material associated with the charge/discharge cycle is suppressed.

Furthermore, when the above-mentioned negative electrode active material absorb lithium ions by charging and become in a highly charged state, they have difficulty in receiving lithium ions. In other words, in the highly charged state, the lithium concentration in the negative electrode active materials is increased, and the interaction between lithium becomes stronger. Therefore, the diffusion of lithium becomes slower in the negative electrode active material and, in particular, becomes in a diffusion controlled state on the surface of the negative electrode active material. Therefore, lithium ions that are not allowed to be received from a non-

aqueous electrolyte into the negative electrode active material may precipitate as metallic lithium on the surface of negative electrode active material layer **11**B, or if received, may be limited to a portion where lithium ions are received easily. As a result, a portion that receives lithium ions and a portion that does not receive lithium ions are mixed unevenly, whereby the composition of the negative electrode active material becomes nonuniform. When the charge/discharge cycle accompanying the production of nonunoform compositions described above is repeated, the cycle life is rapidly degraded. Therefore, in a completely charged state of lithium secondary battery **1** charged by a predetermined charging method, the capacity is controlled so that the negative electrode active material is in a first partially charged state. By controlling in this way, the capacity deterioration of the negative electrode active material associated with the charge/discharge cycle is suppressed. Thus, in a completely charged state of lithium secondary battery **1** charged by a predetermined charging method, the capacity is designed so that the positive electrode active material and the negative electrode active material are in the first partially charged state, respectively.

On the other hand, when lithium secondary battery **1** is in a completely discharged state, when the charged state of the negative electrode active material becomes too low, lithium absorbed and reduced by the negative electrode active material and the non-aqueous electrolyte react with each other, thus destroying a coating film formed on the surface of the negative electrode active material. A part of the absorbed lithium alloys and forms a skeleton structure with Si and Sn. When the charged state of the negative electrode active material becomes low and even the lithium that forms the skeleton structure at the time of discharging is taken out, the negative electrode active material is largely contracted.

In the case of an alloy of Si and Sn, a hysteresis appears. This is because a lithium-rich alloy generated at the time of charging partly remains even at the end of discharge. When the charging state of the partly remaining alloy becomes too low, lithium ions are released, thereby causing a rapid contraction.

Accordingly, the coating film is destroyed. When the coating film is destroyed, the negative electrode active material thus exposed reacts with the non-aqueous electrolyte. This reaction is a side reaction that reduces the battery capacity. When such a side reaction proceeds, the capacity is deteriorated with the advancement of charge and discharge cycles. In this exemplary embodiment, in a completely discharged state of lithium secondary battery **1** discharged by a predetermined discharging method, the capacity is designed so that the negative electrode active material is in a second partially charged state. Therefore, the destruction of the coating film is suppressed and the reaction between the negative electrode active material and the non-aqueous electrolyte is suppressed, and thus the capacity deterioration associated with the charge/discharge cycle is suppressed.

FIG. **2** is a conceptual graph showing a relation between a charged state and resistivity in one example of negative electrode **11** of a lithium secondary battery in accordance with the first exemplary embodiment of the present invention. In this example, $SiO_{0.3}$ is used as a negative electrode active material, but a negative electrode active material containing Si or Sn shows substantially similar tendency. When the charged state is more than 90%, the property of receiving lithium ions is lowered as mentioned above, and the resistivity is increased. On the other hand, when the charged state is less than 10% and discharging proceeds, such a large contraction that destroys the coating film occurs, thereby increasing the resistivity.

Thus, it is preferable that the charged state of the negative electrode active material is 90% or less in the completely charged state of lithium secondary battery **1**. That is to say, it is preferable that the charged state of the negative electrode active material is preferably 90% or less in the first partially charged state. When the amount of lithium ions absorbed by the negative electrode active material is controlled by designing the capacity in this way, the capacity deterioration associated with charge and discharge cycles can be suppressed. That is to say, both battery capacity and charge and discharge cycle characteristics may be satisfied. In a completely charged state of lithium secondary battery **1**, when the charged state of the negative electrode active material is more than 90%, as mentioned above, the precipitation of metallic lithium or nonuniform composition of the negative electrode active material remarkably occurs. Therefore, it is preferable that the charged state of the negative electrode active material is 90% or less in the first partially charged state.

Furthermore, it is preferable that the predetermined charging method for allowing lithium secondary battery **1** to be in a completely charged state may include a method of performing constant-current charging at an electric current value of ⅕ or less of the discharge capacity value of the lithium secondary battery to a predetermined charge end voltage. Even if the charge is carried out at a low rate of electric current in this way, by preventing the negative electrode active material from being charged deeply, the charged state of the negative electrode active material may be controlled reliably.

Furthermore, it is preferable that a capacity is designed in a manner that the charged state of the negative electrode active material becomes 10% or more in a completely discharged state of lithium secondary battery **1**. Designing the capacity in this way may suppress the destruction of the coating film formed on the surface of the negative electrode active material. As a result, the reaction between an exposed negative electrode active material and the non-aqueous electrolyte is suppressed, and the capacity deterioration associated with a charge/discharge cycle may be suppressed. This reaction is a side reaction to reduce the battery capacity. When such a side reaction is suppressed, the capacity deterioration associated with the charge/discharge cycle may be suppressed. That is to say, both battery capacity and the charge/discharge cycle characteristics may be achieved.

Furthermore, it is preferable that the predetermined discharging method for allowing lithium secondary battery **1** to be in a completely discharged state may include a method of performing constant-current discharging at an electric current value of ⅕ or less of the value of the discharge capacity of the lithium secondary battery to a predetermined the charge end voltage. Even if discharge is carried out at a low rate of electric current in this way, by preventing the negative electrode active material from being discharged deeply, the charged state (discharged state) of the negative electrode active material may be controlled reliably.

Next, with reference to FIGS. **3** to **6**, the change in the electrode potential of positive electrode **10** and negative electrode **11** in the course of charging and discharging of lithium secondary battery **1** and the presence state of lithium ions are described. FIG. **3** is a conceptual graph showing the change in the electrode potential of positive electrode **10** and negative electrode **11** when lithium secondary battery **1** in accordance with the first exemplary embodiment of the present invention is charged. FIG. **4** is a conceptual diagram showing the presence state of lithium ions in positive electrode **10** and negative electrode **11** at a charge end point in lithium secondary battery **1** in accordance with the first exemplary embodiment of the present invention. FIG. **5** is a conceptual graph showing the

change in the electrode potential of positive electrode **10** and negative electrode **11** when lithium secondary battery in accordance with the first exemplary embodiment of the present invention **1** is discharged. FIG. **6** is a conceptual diagram showing the presence state of lithium ions in positive electrode **10** and negative electrode **11** at a discharge end point of lithium secondary battery **1** in accordance with the first exemplary embodiment of the present invention. Note here that in this example, the charge end voltage is made to be 4.2 V and discharge end voltage is made to be 3.0 V. In FIGS. **4** and **6**, a hatched portion represents a part in which lithium ions are received and a white portion represents a part that is capable of receiving lithium ions.

Since the discharge end voltage is 3.0 V, a voltage between electrodes (potential difference) before starting charging is somewhat larger than 3.0 V as shown in FIG. **3**. For example, by charging at 0.2 C (electric current of ⅕ of the discharge capacity value), the voltage between electrodes is increased. When the voltage between electrodes reaches 4.2 V, charge is terminated. At this time, as shown in FIG. **4**, lithium ions released from positive electrode **10** are absorbed by negative electrode **11**. Then, at the charge end point, positive electrode **10** is in the first partially charged state in which lithium ions are not completely released, and negative electrode **11** is in the first partially charged state in which it has a capability of absorbing further lithium ions. In other words, negative electrode **11** has a charge reserve that is a capacity region capable of absorbing further lithium ions. When the positive electrode active material is $LiCoO_2$, it has a composition of, for example, $Li_{0.5}CoO_2$ in the charge end state. When the negative electrode active material is $SiO_{0.3}$, it has a composition of, for example, $SiO_{0.3}Li_{4.0}$ in the charge end state.

Next, with reference to FIGS. **5** and **6**, discharge of lithium secondary battery **1** is described. Since the charge end voltage is 4.2 V, the voltage between electrodes before starting discharging is somewhat smaller than 4.2 V as shown in FIG. **5**. For example, by discharging at 0.2 C (electric current of ⅕ of discharge capacity value), the voltage between electrodes is reduced. When the voltage between electrodes reaches 3.0 V, discharge is terminated. At this time, as shown in FIG. **6**, lithium ions released from negative electrode **11** are absorbed by positive electrode **10**. Then, at the discharge end point, negative electrode **11** is in the second partially charged state in which it is able to release further lithium ions. That is to say, negative electrode **11** has a discharge reserve that is a capacity region capable of releasing further lithium ions.

FIG. **6** shows that positive electrode **10** is in a completely discharged state in which lithium ions cannot further be received, but the state is not limited to this alone. If the positive electrode active material is used until it becomes in a completely discharged state, the reaction in positive electrode **10** is a main cause to reduce a voltage, and the voltage is remarkably changed. Thus, discharge end may be detected easily. When the positive electrode active material is $LiCoO_2$, it has a composition of, for example, $LiCoO_2$ in the discharge end state. When the negative electrode active material is $SiO_{0.3}$, it has a composition of, for example, $SiO_{0.3}Li_{1.0}$ in the discharge end state.

Next, a method of setting the capacities of positive electrode **10** and negative electrode **11** in such states is described in various cases mainly with respect to the discharge side. FIGS. **7**A and **7**B are conceptual diagrams showing the presence state of lithium ions when positive electrode **10** in a completely discharged state of the lithium secondary battery and negative electrode **11** in a state without containing lithium ions are used in accordance with the first exemplary embodiment of the present invention. As shown in FIG. **7**A, the positive electrode active material used for positive electrode **10** is generally stable, that is, in a state in which lithium ions cannot be further received when it is synthesized. On the other hand, the negative electrode active material contained in negative electrode **11** has irreversible capacity. When lithium secondary battery **1** is charged from this state, firstly, lithium ions released from positive electrode **10** are consumed so as to compensate the irreversible capacity of the negative electrode active material. Lithium ions in this part cannot be released from negative electrode **11** even if discharge is carried out. Next, lithium ions released from positive electrode **10** are absorbed by the reversible capacity part of the negative electrode active material. Then, as shown in FIG. **7**B, discharge is terminated in the second partially charged state. Thus, the deactivation of the negative electrode active material may be suppressed.

Herein, even if the capacity of positive electrode **10** at the left side from the first partially charged state is larger than the total of the capacity of a range of capacity to be used and the irreversible capacity of negative electrode **11**, discharge is terminated in the charged state of negative electrode **11**. Therefore, a part of the filled amount of the active materials of the positive electrode **10** may be wasted. On the other hand, when the capacity of positive electrode **10** at the left side from the first partially charged state is smaller than the total of the capacity of a range of capacity to be used and the irreversible capacity of negative electrode **11**, the absolute amount of lithium ions contained in lithium secondary battery **1** is reduced. Therefore, the capacities of positive electrode **10** and negative electrode **11** are set respectively in a manner that the capacity of positive electrode **10** at the left side from the first partially charged state is made to be equal to the total of the capacity of a range of capacity to be used and the irreversible capacity part of negative electrode **11**.

In this case, it is preferable that the second partially charged state of the negative electrode active material is set to 10% or more with respect to the entire capacity of the negative electrode active material excluding the irreversible capacity. However, when such positive electrode **10** and negative electrode **11** are used, it is necessary to terminate discharge in a state in which positive electrode **10** has an ability to receive lithium ions. That is to say, it is necessary to terminate discharge in a state in which the battery voltage is relatively high.

Next, a case where negative electrode **11** is provided with an irreversible capacity of lithium in advance when the battery is assembled is described. FIG. **8** is a conceptual diagram showing presence state of lithium ions when positive electrode **10** in a completely discharged state and negative electrode **11** provided with lithium in advance are used in another lithium secondary battery in accordance with the first exemplary embodiment of the present invention. In this case, an irreversible capacity and a discharge reserve are compensated with lithium to be provided. Then, the amounts of the positive electrode active materials and the negative electrode active materials to be filled are designed in a manner that the ranges of capacity to be used of positive electrode **10** and negative electrode **11** are equal to each other. Thus, lithium secondary battery **1** excellent in the charge/discharge cycle characteristics may be produced in which the deactivation of the negative electrode active materials is suppressed while the capacity of lithium secondary battery **1** is maximized.

When the capacities of negative electrode **11** and positive electrode **10** are designed in this way, it is preferable that lithium is provided to negative electrode **11**. With such a method, it is possible to control easily the combination of charged states of the negative electrode active material and

the positive electrode active material and to maximize the capacity of lithium secondary battery **1**.

Next, a case where lithium of the irreversible capacity of negative electrode **11** is provided to negative electrode **11** in advance when the battery is assembled, and where positive electrode **10** also has the irreversible capacity is described. FIGS. **9**A and **9**B are conceptual diagrams showing the presence state of lithium ions when positive electrode **10** having irreversible capacity and negative electrode **11** provided with lithium in advance are used in still another lithium secondary battery in accordance with the first exemplary embodiment of the present invention. In this case, as shown in FIG. **9**A, the amount of lithium to be provided to negative electrode **11** is made to be smaller than that in the case of FIG. **8** by an amount of the irreversible capacity. When lithium secondary battery **1** is charged from this state, lithium ions released from positive electrode **10** are absorbed by the reversible capacity of the negative electrode active materials. Then, as shown in FIG. **9**B, on discharging, positive electrode **10** cannot receive further lithium ions when the irreversible capacity is remained. Then, the capacity is set in a manner that the irreversible capacity of positive electrode **10** and the lithium provided to negative electrode **11** compensate the irreversible capacity and discharge reserve of negative electrode **11**. Thus, the deactivation of the negative electrode active material is suppressed.

Note that, in an alkaline storage battery using a hydrogen absorbing alloy for a negative electrode, the capacities of the positive electrode and the negative electrode are designed in a manner that a discharge reserve is provided. However, when a hydrogen absorbing alloy is used for the negative electrode, the components of the hydrogen absorbing alloy are eluted if the negative electrode is discharged excessively, so that the discharge reserve is provided. Thus, the mechanism is different from that of this exemplary embodiment.

Second Exemplary Embodiment

In this exemplary embodiment, an additive for improving the viscosity of a coating film of a negative electrode active material is added to lithium secondary battery **1**. Except the additive, the configuration of the battery and idea of designing the capacity in this exemplary embodiment are substantially similar to those of the first exemplary embodiment.

As the additive, vinylene carbonate, vinyl ethylene carbonate, fluoroethylene carbonate and the like may be used singly or in combination thereof. These additives may be added to an electrolytic solution as a non-aqueous electrolyte or applied to negative electrode **11** prior to the infusion of the electrolytic solution. Since the use of such additives improves the viscosity of the coating film of the negative electrode active material, the destruction of the coating film when discharge proceeds and the charged state of the negative electrode active material is lowered is suppressed. Due to this, when the second partially charged state is made to be the same as the state before addition, the capacity deterioration of the negative electrode active material associated with charge and discharge cycles may be still more suppressed.

Furthermore, the second partially charged state may be made to 5% or less. Since the destruction of the coating film is suppressed, even if the negative electrode active material is further discharged to the completely discharged side, the capacity deterioration of the negative electrode active material associated with the charge/discharge cycle becomes the same as that before addition. Since the utilization efficiency of the negative electrode active material is improved in this way, the capacity of lithium secondary battery **1** may be increased.

In the above description, an example of the battery using plate positive electrode **10** and negative electrode **11** is described. However, the description is not limited to this example alone. It may be applied to a cylindrical or rectangular battery in which positive and negative electrodes are wound. Furthermore, it may be applied to a coin type battery in which an active material layer is formed directly to a case without using a current collector.

EXAMPLE

Hereinafter, specific examples and the effects thereof are described. Firstly, a production procedure of negative electrode **11** is described. FIG. **10** is a schematic configuration view showing a manufacturing device of a negative electrode for a non-aqueous electrolyte secondary battery in the Example of the present invention. FIG. **11** is a schematic sectional view showing a negative electrode produced by using the device of FIG. **10**.

Manufacturing device **80** includes: vapor deposition unit **85** for forming a columnar body by depositing, on the surface of current collector **11**A, material to be vacuum-deposited; gas introducing pipe **82** for introducing oxygen into vacuum chamber **81**; and fixing stand **83** for fixing current collector **11**A. At the tip of gas introducing pipe **82**, nozzle **84** for supplying oxygen into vacuum chamber **81** is provided. These are disposed in vacuum chamber **81**. Vacuum pump **86** reduces the pressure inside vacuum chamber **81**. Fixing stand **83** is disposed above nozzle **84**. Vapor deposition unit **85** is disposed below perpendicular to fixing stand **83**. Vapor deposition unit **85** includes an electron beam as a heating part and a crucible in which vapor deposition raw materials are disposed. In manufacturing device **80**, the position relation between current collector **11**A and vapor deposition unit **85** can be changed depending upon the angle of fixing stand **83**.

Next, a procedure for forming a columnar body made of SiO_x and having a bending point on current collector **11**A is described. Firstly, 30 μm-thick band-like electrolytic copper foil is used as a base material, convex parts **11**C each having a height of 7.5 μm and a width of 10 μm are formed on the surface of the base material by plating. Thus, current collector **11**A on which convex parts **11**C are formed in the intervals of, for example, 20 μm is prepared. Then, current collector **11**A is fixed on fixing stand **83** shown in FIG. **10**.

Next, fixing stand **83** is set in a manner that the normal line of current collector **11**A directs at an angel of ω° (for example, 55°) with respect to the incident direction from vapor deposition unit **85**. Then, for example, Si is heated by an electron beam so as to evaporate and allowed to enter the convex portion **11**C of current collector **11**A. At the same time, oxygen is introduced from gas introducing tube **82** and supplied from nozzle **84** to current collector **11**A. That is to say, the inside of vacuum chamber **81** is made to be an atmosphere of oxygen of the pressure of, for example, 3.5 Pa. Thus, SiO_x, which is made by combining Si and oxygen, is deposited on convex portions **11**C of current collector **11**A. The columnar body portion **87**A in a first stage is formed to the predetermined height (thickness). At this time, by adjusting the amount of oxygen gas to be introduced, the value x in SiO_x may be controlled.

Next, as shown in a broken line of FIG. **10**, fixing stand **83** is rotated so that the normal line direction of current collector **11**A is located at the position of the angle (360−ω)° (for example, 305°) with respect to the incident direction from

vapor deposition unit **85**. Then, Si is evaporated from vapor deposition unit **85** and allowed to enter columnar body portion **87**A in the first stage of current collector **11**A from the direction opposite to the direction in which columnar body portion **87**A extends. At the same time, oxygen is introduced from gas introducing tube **82** and supplied to current collector **11**A from nozzle **84**. Thus, SiO_x is formed as columnar body portion **87**B in a second stage to a predetermined height (thickness) on columnar body portion **87**A in the first stage.

Next, fixing stand **83** is returned to an original state and columnar body portion **87**C in a third stage is formed on columnar body **87**B to a predetermined height (thickness). Thus, columnar body portion **87**B and columnar body portion **87**C are formed in a manner that their obliquely rising angles and obliquely rising directions are different from each other. Columnar body portion **87**C is formed in the same direction as columnar body portion **87**A. Thus, active material lump **87** including three stages of columnar body portions is formed on current collector **11**A. Thus, active material layer **11**B may be formed. By adjusting the amount of introduced oxygen gas in each stage, the value x in SiO_x in each stage may be controlled, respectively.

In the above description, active material lump **87** including three stages of columnar body portions is described. However, in this Example, by repeating the adjustment of angles of fixing stand **83**, a columnar body including 30 stages of columnar body portions is formed. The obliquely rising direction of each stage of columnar body including 30 stages can be controlled by changing angle ω of the normal direction of the surface of current collector **11**A with respect to the incident direction from vapor deposition unit **85**. Furthermore, the value x in SiO_x of each stage can be controlled in the range from 0.1 or more and less than 2. In the below-mentioned consideration, the average value of entire active material lump **87** is defined as the value x.

Next, a procedure for providing lithium to an active material layer of negative electrode **11** is described with reference to FIGS. **12** and **13**. FIG. **12** is a schematic configuration view showing a vacuum evaporator for providing a negative electrode with lithium in an Example of the present invention, and FIG. **13** is a conceptual sectional view showing a configuration of a lithium vapor deposition nozzle of the vacuum evaporator of FIG. **12**. This device includes copper crucible **24** into which rod heater **23**A serving as a heating part is incorporated, lithium vapor deposition nozzle **25**, vacuum chamber **20**, and vacuum pump **31**. Lithium vapor deposition nozzle **25** restricts the movement route of the generated lithium vapor and provides lithium to the surface of negative electrode **11** by using a lithium vapor. Vacuum chamber **20** accommodates negative electrode **11**, the heating part and lithium vapor deposition nozzle **25**. This device further includes gas nozzle **26** and gas flow controller **27**. Gas nozzle **26** opens toward the inside of lithium vapor deposition nozzle **25** and allows gas to flow into the movement route of lithium vapor. Vacuum pump **31** reduces the pressure inside vacuum chamber **20**.

Firstly, as shown in FIG. **13**, negative electrode **11** is disposed in a manner that it is forwarded from feeding roll **21** in vacuum chamber **20** to winding-up roll **30** via cooling CAN **22** cooled to, for example, 20° C. Then, metallic lithium is placed in copper crucible **24** into which rod heater **23**A is incorporated, and lithium vapor deposition nozzle **25** into which rod heater **23**B is incorporated is assembled to copper crucible **24**. In this state, the pressure inside vacuum chamber **20** is reduced to, for example, 3×10^{-3} Pa. That is to say, the pressure of an atmosphere including negative electrode **11** and a supply source of lithium is reduced. Then, in order to generate lithium vapor, electricity is applied to rod heater **23**A to heat lithium **29**A that is placed in copper crucible **24** and serves a vapor supplying source. Furthermore, it is preferable that electricity is also applied to rod heater **23**B in order to avoid cooling of vapor inside lithium vapor deposition nozzle **25** and depositing of lithium. The temperatures of copper crucible **24** and lithium vapor deposition nozzle **25** are controlled to be, for example, 580° C. by monitoring the temperatures with thermocouple **28**. Herein, lithium vapor deposition nozzle **25** limits the movement route of a lithium vapor. The lithium vapor is supplied to negative electrode **11** via lithium vapor deposition nozzle **25**, so that an active material layer of negative electrode **11** is provided with lithium. By limiting the movement route of the lithium vapor in this way, the lithium vapor may be supplied to the active material layer efficiently. Then, for example, by adjusting the speed at which negative electrode **11** is forwarded from feeding roll **21** to winding-up roll **30**, the amount of lithium to be provided per unit area of negative electrode **11** may be controlled. That is to say, when SiO_x provided with lithium is expressed by Li_a-SiO_x, the value a in Li_aSiO_x may be controlled.

By changing the value x and the value a in Li_aSO_x variously, eleven kinds of negative electrodes **11** are produced and represented by negative electrode **11** of samples A to K. The combinations of the value x and the value a in samples A to K include: A: (0.2, 0), B: (0.4, 0), C: (0.6, 0), D: (0.6, 1.2), E: (0.5, 1.0), F: (0.4, 0.8), G: (0.2, 1.0), H: (0.2, 0.4), I: (0.1, 0.6), J: (0.1, 0.2), and K: (0.5, 0.2).

On the other hand, positive electrode **10** is produced as follows. Firstly, 10 parts by weight of acetylene black as a conductive agent and 5 parts by weight of polyvinylidene fluoride as a binding agent are mixed with 85 parts by weight of lithium nickelate ($LiNiO_2$) powder. These are dispersed in dehydrated N-methyl-2-pyrrolidone to prepare slurry of a positive electrode mixture material. This positive electrode mixture material is applied to positive electrode current collector **10**A made of aluminum foil, dried, then rolled out, and cut into a predetermined dimension. Thus, positive electrode **10** is produced. The thus produced positive electrode active material layer **10**B of positive electrode **10** has a density of 3.3 g/cm^3 and a thickness of about 56 μm.

On the other hand, 1 wt % vinylene carbonate is added to the mixture solvent containing ethylene carbonate and ethyl methyl carbonate in a volume ratio of 1:3, and furthermore, $LiPF_6$ is dissolved at the concentration of 1.0 mol/L so as to prepare a non-aqueous electrolytic solution.

Next, positive electrode lead **14** made of aluminum is attached to positive electrode current collector **10**A, and negative electrode lead **15** made of nickel is attached to negative electrode current collector **11**A. Thereafter, positive electrode **10** and negative electrode **11** are interposed onto each other via separator **12** made of polypropylene microporous membrane so as to form an electrode group. At this time, positive electrode active material layer **10**B is allowed to face negative electrode active material layer **11**B. Then, the electrode group is inserted into outer case **13** in a manner that one ends of positive electrode lead **14** and negative electrode lead **15** are exposed from outer case **13** made of aluminum laminate, and then, the non-aqueous electrolytic solution is injected. Thereafter, the pressure inside outer case **13** is reduced and seals the opening portion of outer case **13** by heat melting. Thus, lithium secondary batteries of samples A to K are completed. Since the capacity density is changed depending upon the value x in SiO_x, the thickness of negative electrode active material layer **11**B is changed depending upon the capacity of positive electrode **10**. Herein, in samples D to

J, the charged state of the negative electrode active material is made to be 10% in a completely discharged state of the lithium secondary battery.

The discharge capacity and cycle retention ratio of the thus produced lithium secondary battery are evaluated. In evaluating the discharge capacity, firstly, electric current is made to be 1 CmA and constant-current charge is carried out to end voltage of 4.2 V. Herein, 1 CmA corresponds to an electric current at which the design capacity of positive electrode **10** is charged or discharged for one hour. Thereafter, discharge is carried out in the conditions of 1 CmA and the end voltage of 2.5 V. Next, constant-current charge is carried out in the conditions of 1 CmA and the end voltage of 4.2 V, and then charge is carried out at a constant voltage of 4.2 V until the electric current value is lowered to 0.1 CmA. Then, a constant-current discharge is carried out in the conditions of 1 CmA and the end voltage of 2.5 V. At this time, the discharge capacity is calculated and the ratio thereof with respect to the design capacity of positive electrode **10** is calculated.

Furthermore, when this discharge capacity is defined as 100%, the capacity retention ratio of the battery after 500 cycles has carried out under the above-mentioned charging and discharging conditions is calculated and the calculated value is defined as a cycle retention ratio. Furthermore, the battery after the cycle test is disassembled and negative electrode **11** is observed. The value x and value a in negative electrode **11** of each sample are shown in FIG. **14**, and the obtained results are shown in Table 1, respectively.

TABLE 1

sample	value x	value a	Discharge capacity ratio (%)	Cycle retention ratio (%)	Disassembled findings
A	0.2	0	98	30	normal
B	0.4	0	84	40	normal
C	0.6	0	65	50	normal
D	0.6	1.2	100	81	normal
E	0.5	1.0	100	80	normal
F	0.4	0.8	100	78	normal
G	0.2	1.0	92	75	somewhat expansion
H	0.2	0.4	100	75	normal
I	0.1	0.6	99	72	minor peeling and somewhat expansion
J	0.1	0.2	100	70	minor peeling
K	0.5	0.2	82	75	normal

As is apparent from Table 1, the discharge capacity is small in samples A, B and C. This is because lithium is not provided to negative electrode **11**. Therefore, since a stable coating is not formed on active material lump **87**, the cycle retention ratio is also small. In sample D on line **41** in FIG. **14**, since lithium is provided, the discharge capacity is remarkably increased as compared with sample C. However, since the value x is large, it is necessary to increase the thickness of negative electrode active material layer **11**B, and a battery having a sufficient energy density cannot be obtained. Line **41** represents the relation: a=2x.

Samples E, F, H, and J on line **41** show the same discharge capacity. Since the negative electrode active material layer **11**B becomes thinner as the value x is smaller, the energy density becomes larger in this order. However, as the value x is smaller, the change in volume of the negative electrode active material associated with charge and discharge is increased. Therefore, the cycle retention ratio is reduced in this order, and the cycle retention ratio in sample J is somewhat small. Furthermore, according to the disassembled finding, minor peeling of negative electrode active material layer **11**B is observed.

In sample K having the same value a as that of sample J and the same value x as that of sample E, the cycle retention ratio is in the middle between that of sample J and that of sample E. Furthermore, since sample K has the value a smaller than that of sample E, it has the energy density smaller than sample E, but shows the same level of energy density as that of sample B.

Line **42** is a boundary line of the preferable combination of value x and value a disclosed in WO2007/010922 pamphlet. Sample G is in the boundary line of this preferable range, and sample I is in an extended line of the lower limit line of line **42** and corresponds to value x in sample J. The lower limit line of line **42** shows the relation: a=x+0.5.

Sample G is in a region in which the value x is small, for example, x=0.2. In this region, when lithium is provided until a=1.0 is satisfied, the charge reserve shown in FIG. **4** is also charged at the time of charging. Consequently, the expansion of negative electrode active material layer **11**B at the time of charging is increased. As a result, the cycle retention ratio is somewhat lowered.

On the other hand, sample I shows the same level of the discharge capacity and the cycle retention ratio as those of sample J. However, since the amount of lithium to be provided is larger than sample J, similar to sample G, the expansion of negative electrode active material layer **11**B at the time of charging is increased. Also, the disassembled finding shows minor peeling in negative electrode active material layer **11**B and little bit expansion. Although these samples have smaller value x than that of sample G, the cycle retention ratio is the same level as that of sample G.

Thus, in this Example, in the region in which the value x is small, it is attainable to find more preferable combination of value x and value a as compared with the combination disclosed in WO 2007/010922 pamphlet.

From the above-mentioned results, in a region above line **42** in which $0.1 \leq x \leq 0.5$ is satisfied, that is, when the amount of lithium to be provided is larger than that of line **42**, the charge depth is increased and the expansion of active material lump **87** is increased. Therefore, it is assumed that the cycle characteristic is lowered. Furthermore, in a region of a <0.2, in particular, when a is 0, the amount of lithium to be provided is reduced and the expansion of active material lump **87** is reduced, however, a stable coating film is not formed on active material lump **87**. Therefore, it is assumed that the cycle characteristic is lowered.

Furthermore, in the range of $x<0.1$, since the expansion of SiO_x itself constituting active material lump **87** is increased, it is assumed that active material layer **11**B tends to peel from current collector **11**A and thereby the cycle characteristic is reduced. On the contrary, in the range of $x>0.5$, the energy density is reduced.

Therefore, when $0.1 \leq x \leq 0.5$ is satisfied in SiO_x and lithium is provided to SiO_x to thus form Li_aSiO_x, it is preferable that $0<a \leq (x+0.5)$ is satisfied. More preferably, $0.2 \leq a \leq (x+0.5)$ is satisfied, and further more preferably, $2x \leq a \leq (x+0.5)$ is satisfied.

Next, the effect of additives is described taken sample H as an example. As shown in Table 1, the cycle retention ratio of sample H is 75%. Samples L, M and N are prepared by adding 2 wt. % of additives to the non-aqueous electrolytic solution of a lithium secondary battery that is the same as sample H. In sample L, vinylene carbonate is added; in sample M, vinyl ethylene carbonate is added; in sample N, fluoroethylene carbonate is added, respectively. When the cycle retention

ratios of these samples are evaluated as mentioned above, they are 80%, 77%, and 80%, respectively. In this way, by allowing the additives for improving the viscosity of the coating film of the negative electrode active material to be contained in the lithium secondary battery, the capacity deterioration associated with the charge/discharge cycle may be suppressed.

Note here that in sample H, as mentioned above, in a completely discharged state of the lithium secondary battery, the capacity of negative electrode **11** is selected with respect to positive electrode **10** in a manner that the charged state of the negative electrode active material is 10%. Then, sample P with 2 wt. % addition of vinylene carbonate and sample Q with 2 wt. % addition of fluoroethylene carbonate are prepared in a manner that the charged state of the negative electrode active material is allowed to become 5% in a completely discharged state of the lithium secondary battery by reducing the amount of lithium to be provided. When the cycle retention ratios of samples P and Q are evaluated by the above-mentioned method, both rates are 75%. Thus, when the additive is used, the lower limit of the charged state of the negative electrode active material in a completely discharged state of lithium secondary battery may be lowered while the cycle characteristic is maintained. Therefore, the battery capacity may be increased.

INDUSTRIAL APPLICABILITY

A lithium secondary battery of the present invention includes a positive electrode having a positive electrode active material absorbing and releasing lithium ions, a negative electrode having a negative electrode active material containing at least one element selected from the group consisting of silicon and tin, and a lithium ion conducting electrolyte. In such a lithium secondary battery, the capacities of the positive electrode and negative electrode are selected in a manner that in a completely charged state of the lithium secondary battery charged by a predetermined charging method, the positive electrode active material and the negative electrode active material are in a first partially charged state, respectively, and in a completely discharged state of the lithium secondary battery discharged by a predetermined discharging method, the negative electrode active material is in the second partially charged state. By designing the battery in this way, a lithium secondary battery usable for a long time is provided.

The invention claimed is:

1. A lithium secondary battery, comprising:

a positive electrode having a positive electrode active material for absorbing and releasing a lithium ion;

a negative electrode having a current collector and a negative electrode active material provided on the current collector, the negative electrode active material including at least one of silicon oxide and tin oxide; and

a non-aqueous electrolyte having lithium ion conductivity and being interposed between the positive electrode and the negative electrode,

wherein a completely charged state of the lithium secondary battery is defined by the positive electrode active material and the negative electrode active material charged at a first partially charged level at which the negative electrode active material is in an around 90% charged state,

a completely discharged state of the lithium secondary battery is defined by a second partially charged state at which the negative electrode active material is in an around 10% charged state, and

the negative electrode active material has lithium vapor-deposited thereon to adjust the second partially charged level, wherein an amount of the lithium vapor-deposited on the negative electrode active material is less, by an amount of an irreversible capacity of the positive electrode active material, than an amount necessary to adjust the second partially charged state of the negative electrode active material to the around 10% charged state if the positive electrode active material did not have the irreversible capacity, and

further wherein the negative electrode active material is made mainly of SiO_x ($0.1 \leq x \leq 0.5$), which is made into Li_aSiO_x ($0 < a \leq (x+0.5)$) by vapor-depositing lithium on the negative electrode.

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